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Holographically fabricated photonic crystals with large reflectance

Y. C. Chen,[a] J. B. Geddes III, J. T. Lee,[a] P. V. Braun,[a] and P. Wiltzius[a),b)]
Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

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We report reflection and transmission spectra from three-dimensional polymer photonic crystals fabricated by holographic lithography. The measured peak reflectance matches that predicted by both a finite-difference time-domain method a simple transfer matrix theory and is ~70%, significantly higher than previous reports of ~30% reflectance. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2820449]

Holographic lithography is one of the most promising techniques for the fabrication of three-dimensional (3D) photonic crystals.[1,2] In this method, the periodic patterns of the crystals are generated and recorded in photosensitive materials via interference of multiple coherent laser beams. This technique is attractive due to its versatility in creating different crystalline symmetries and bases, facilitating the experimental demonstration of various structures.[3–7] Holographically defined polymer photonic crystals can serve as templates for subsequent deposition of high refractive index materials for applications requiring a pseudo- or a complete photonic band gap.[8,9] To incorporate functionality using the band gap, controlled defects can be placed into the crystals via multiphoton polymerization either by using the same photoresist before hologram development or by infiltrating the developed structure with other recordable media.[10,11]

Holographic photonic crystals are expected to exhibit excellent optical properties due to their large areas and defect-free nature. However, reported reflectances of typical fabricated crystals are not as high as expected from theoretical considerations, only about 30% for polymeric templates,[8,9,12,13] while reflectances from self-assembled colloidal crystals can exceed 70%.[14] The moderate optical response of the polymer holograms sets an upper bound on the optical properties of structures and optical components formed via replication with high dielectric constant materials.

In this letter, we present a significant improvement to the optical response of holographically fabricated photonic crystals—manifested as an increase in reflectances. Theoretical reflectance spectra were calculated with both a finite-difference time-domain (FDTD) method and a simple one-dimensional (1D) transfer matrix method based on the theoretical structure found from optical measurements and scanning electron microscopy (SEM). The calculated spectra match well with experimental spectra, indicating that good crystal quality is achieved. We also demonstrate that the 1D transfer matrix method is several orders of magnitude faster than FDTD and is a useful tool when a full FDTD computation is not practical.

A continuous-wave, frequency-doubled $Nd:YVO_4$ laser (532 nm) was used for holographic exposure. The laser beam was split into four of equal intensity and arranged in an "umbrella" geometry.[2] To compensate for resist shrinkage perpendicular to the substrate, we chose to create an elongated interference pattern.[15] The angle between the central beam and the side beams was 58.78° in air, corresponding to 32.15° inside the unexposed photoresist with refractive index of 1.607 at 532 nm, as determined by spectroscopic ellipsometry. Prism coupling was not necessary for this setup. The central beam was circularly polarized, and the side beams were linearly polarized in their incident planes.[4] The photoresist had a 0.3 wt % solid content of photoinitiator benzenecyclopentadienyliron(II) hexafluorophosphate (Aldrich) and the remainder SU8 monomer. It was spun coated onto a glass substrate which previously had been coated with a 0.75 μm cured SU8 layer for adhesion promotion. The film was exposed with a 60–90 J cm^{-2} (2–3 s) dose over a spot size of 4 mm. After exposure, it was postbaked at 85 °C for 25 min in dry air then developed in propylene glycol methyl ether acetate for 2 h followed by rinsing in isopropanol and super critically drying with CO_2.

The developed structure has fcc-like symmetry with the (111) plane parallel to the substrate. Figure 1(a) presents a cleaved cross section and Figs. 1(b) and 1(c) cross sections were exposed using focused ion beam milling (FIB). To prevent polymer deformation during ion milling, the sample was coated with a 2 nm layer of Al_2O_3 by atomic layer deposition.

Figure 2(a) shows optical spectra taken from the fabricated crystal with Fourier-transform infrared spectroscopy. The reflectance measurement was normalized to a silver mir-

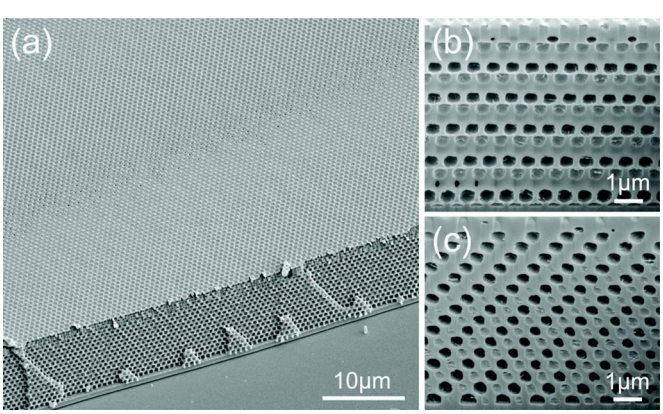

FIG. 1. (Color online) (a) Scanning electron micrographs of a holographic polymer photonic crystal. [(b) and (c)] Cross sectional images obtained from focus ion beam milling. The viewing angle is 52°.

[a)]Also at: Department of Materials Science and Engineering.
[b)]Also at: Department of Physics. Electronic mail: wiltzius@uiuc.edu.

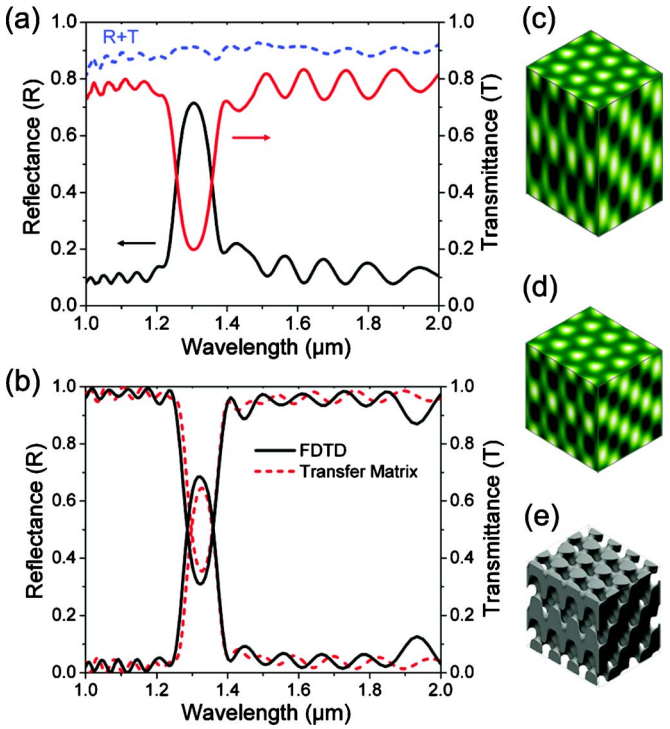

FIG. 2. (Color online) (a) Reflection and transmission spectra of the fabricated photonic crystal in the [111] direction. (b) Simulation result from the transfer matrix method (dotted) and FDTD (solid). (c) Intensity distribution calculated from beam parameters. (d) Shrinkage incorporated gradient for thresholding. (e) Thresholded polymer-air crystal.

ror and transmittance was normalized with air as 100%. The 70% peak in reflection and a transmission dip of 20% at 1.3 μm arise from the internal periodicity, and the periodic oscillations are Fabry-Pérot fringes arising from interference between reflections from the film's interfaces. Transmittance plus reflectance is about 90% over the measured bandwidth.

To rationalize the experimental spectra, a model structure was constructed. First, the intensity distribution was calculated from the beam parameters [Fig. 2(c)]. A 32% shrinkage perpendicular to the substrate resulting in a vertical spacing of 488 nm, as measured by SEM, was incorporated into the intensity profile by resampling the array along the [111] direction. This modified intensity profile [Fig. 2(d)] served as a gradient for a binary threshold filter, the threshold for which was determined by the polymer filling fraction, which in turn depends on the effective refractive index n_e of the structure. We found n_e to be 1.364 from the resonance orders of the Fabry-Pérot fringes which are proportional to wavenumber and film thickness. From n_e, the filling fraction f of the polymer was computed from an effective medium relationship as

$$n_e = \sqrt{f n_p^2 + (1-f) n_a^2}, \tag{1}$$

where $n_a = 1$ and $n_p = 1.57$, obtained by measuring the Fabry-Pérot fringes between 1.1 and 2.1 μm of a cross-linked SU8 film of known thickness. With $n_e = 1.364$, f was determined to be 0.588 and the binary threshold for the modified intensity gradient was then set to match the filling fraction. Intensities greater than the threshold were taken to be polymer, and air filled the remainder [Fig. 2(e)].

The reflectance and transmittance spectra were then computed from the constructed structure using the FDTD method,[16] as implemented in a freely available software package that uses subpixel smoothing algorithms to increase accuracy.[17] The theoretical structure [Fig. 2(e)] was constructed in the software with a 24 nm pixel size resolution; an adhesion layer and a glass half-space substrate were included. The calculated spectra were plotted as the solid line in Fig. 2(b).

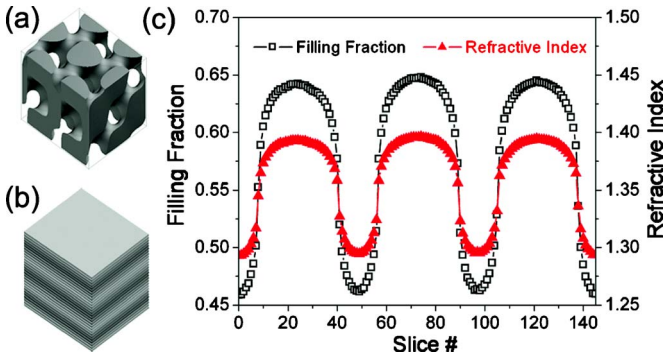

FIG. 3. (Color online) (a) The theoretical 3D structure is approximated (b) as a stack of layers. (c) The filling fraction of each layer determines its effective refractive index.

For a 3D structure with multiple layers and a unit cell of arbitrary shape, as common for holograms, FDTD requires considerable computational power. For this reason, a 1D transfer matrix method was also investigated for calculating the reflection and transmission spectra from the theoretical structure in the [111] direction.[18] The 3D structure was approximated as a stack of 10 nm thick homogeneous slices in the (111) planes, and the effective refractive index of each slice was calculated with Eq. (1) from the filling fraction of polymer within the slice. Both the adhesion layer and the glass substrate halfspace were incorporated into the calculation. Figure 3 presents the periodic variation of filling fraction with depth, which results in a periodic variation of effective refractive index. The reflection and transmission spectra were computed from the thicknesses and refractive indexes of the slices using a common transfer matrix formalism.[19–21] The result is presented as the dotted line in Fig. 2(b). It closely matches the FDTD result, indicating that the 1D transfer matrix method is a valid approximation. Moreover, the transfer matrix computation takes minutes to complete while the FDTD computation takes days.

By comparing Figs. 2(a) and 2(b), it can be seen that the experimental and calculated spectra match quite well in both peak position and peak magnitude. The position of the main peak in the experimental spectra is only 2.5% different than the calculated spectra, within the 5% error of film thickness measurement by SEM. It should be noted that the experimental main peak was not used for constructing the theoretical structure. Slight peak broadening of the experimental peak indicates some variation from perfect periodicity in the structure, which can be expected from any fabrication method. The experimental spectra have a larger background than predicted due to reflection from the back side of the substrate.

One reason for the significant increase in peak reflectance for our holographic crystal, as compared to previous efforts, is low absorption by our photoresist system. Rumpf and Johnson reported that the absorption of the recording film causes chirping of the resulting structures, which in turn lowers their reflectances.[22] In our case, there was a negligible absorption by the SU8 monomer at the laser wavelength of

532 nm, as opposed to the illumination at ultraviolet wavelengths. Virtually, all the absorption in our system was from the photoinitiator, which is similar in design to Irgacure 261[23,24] and exhibits a very low absorption at 532 nm while possessing sufficient photosensitivity. At a 0.3 wt % initiator solid content, the absorption through a 10 μm film was only 2% at 532 nm.

Laser beam quality is also important for characteristics of the fabricated crystals. The laser beam was expanded to reduce intensity variation over its diameter and cleaned with a spatial filter; all optical components were carefully cleaned and the beam was profiled after each component to ensure quality. The Gaussian beam's intensity dropped approximately 10% from its center to a radius of 1 mm. In our typical holograms, the middle 1–2 mm diameter portion exhibited high reflectivity.

In conclusion, we obtained high quality photonic crystals by holographic lithography. Optimization of the photoresist initiation system led to a significant increase in peak reflectance as compared with previously reported holograms. We constructed a 3D representation of the crystal structure from SEM and optical spectroscopy, and showed close agreement between the measured and the calculated spectra from both FDTD and 1D transfer matrix methods. The latter can be used with acceptable accuracy in a small fraction of the time required by the former. Current thick photoresist systems for holographic photonic crystal fabrication exhibit nonnegligible shrinkage perpendicular to the substrate. We believe our approach to shrinkage compensation by fabricating elongated structures and simulating optical spectra with shrinkage incorporated provides a good pathway to explore the optical properties of symmetric holographic photonic crystals with the ultimate goal of manufacturing devices from them.

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